# Measurement of complex $\chi^{(3)}$ using degenerate four-wave mixing with an imaged 2-D phase grating

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**Abstract:** We present a simple optical arrangement for phase sensitive detection of degenerate four-wave mixing (DFWM) to characterize the real and imaginary parts of $\chi^{(3)}$ using an imaged 2-D phase grating. Phase sensitive coherent detection of DFWM signal is demonstrated. Phase stabilization of the interferometric arms is obtained passively with the 2-D grating. A processable polyacetylene sample is characterized at a wavelength of 1.5 $\mu$m using this technique. The observed nonlinearity is determined to be a fast (<250 fs) effect using a simple test.



**OCIS codes:** (190.4380) Nonlinear optics, four-wave mixing; (300.6290) Spectroscopy, four-wave mixing

## References and links

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## 1. Introduction

Characterization of both the magnitude and the phase of the third-order susceptibility, $\chi^{(3)}(\omega;\omega,\omega,-\omega)$ is important for potential device applications of a given nonlinear material. A common characterization technique is the Z-scan method [1]. However, Z-scan technique provides no information about the time scale of the measured nonlinearity. The other common technique is the degenerate four-wave mixing (DFWM) technique [2,3], which is a sensitive technique for studies of the $\chi^{(3)}$ of nonlinear materials, and can be used to perform time-resolved studies of the nonlinearity. Typically, the measured signal is proportional to $|\chi^{(3)}|^2$, but the phase of $\chi^{(3)}$ is not available. Additional measurements are needed to determine the real and imaginary parts of $\chi^{(3)}$ using the DFWM technique, such as the phase-mismatched DFWM method [4]. Another demonstrated technique is the optical Kerr gate (OKG). In the standard OKG, both the induced birefringence and dichroism due to the real and imaginary parts of $\chi^{(3)}$ contribute to the detected signal and can not be seperated. It has been demonstrated that the complex $\chi^{(3)}$ can be determined by appropriate polarization analysis in the modification know as the heterodyne Kerr gate technique [5].

Another alternative is coherent detection of the DFWM signal in which a reference field is mixed coherently on the detector with the DFWM signal [6]. This approach potentially offers the advantage of improved signal-to-noise ratio over direct detection, and the full complex value of the signal can be obtained by varying the phase of the reference field. The main difficulty in implementing this scheme is maintaining the relative phase between the reference and the signal, which could add considerable complexity to experiments. Recently, optical heterodyne detection spectroscopy using diffractive optical elements for passive phase stabilization has been proposed and demonstrated by several groups [7-9]. In these schemes, one-dimensional (1-D) diffraction gratings are used to diffract both pump and probe beams for excitation and detection of laser-induced gratings.

In this paper, we present a simple optical arrangement for direct and coherent detection of DFWM signal utilizing a two-dimensional (2-D) phase grating for characterization of the complex value of $\chi^{(3)}$. The nonlinear refractive index and nonlinear absorption coefficient of a processable polyacetylene polymer sample are characterized using this technique at a wavelength of 1.5 $\mu$m. A simple test shows that the observed nonlinearity is a fast (<250 fs) effect.

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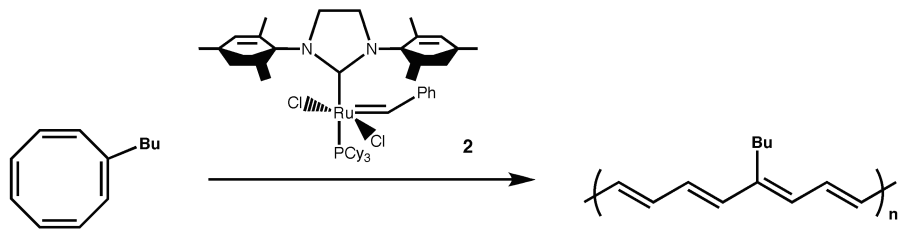


Fig. 1. Ring opening metathesis polymerization method used to synthesize the polyacetylene polymer.

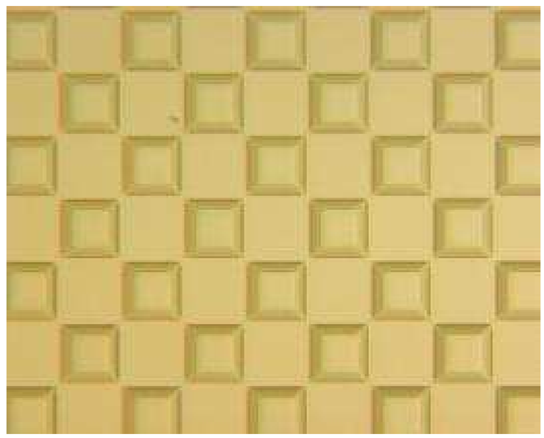

Fig. 2. Optical microscope image of the 2-D phase grating fabricated on a quartz plate.

## 2. Polymer sample

As shown in Fig. 1, an alkyl-substituted polyacetylene polymer **3** was synthesized by the method of ring opening metathesis polymerization (ROMP) [10] with an n-butyl cyclooctatetraene **1** liquid-phase monomer and $2^{nd}$ generation Grubbs catalyst [10] **2** in an inert atmosphere. During polymerization, the monomer/catalyst mixture was transferred to a glass substrate with a 100 $\mu$m thick circular Teflon spacer and a second glass slide was placed on top to permit hermetic sealing of the sandwiched film to avoid oxidation. The refractive index of the film was estimated to be $\sim$2.2 in the near infrared spectral region from interference fringes in its linear absorption spectrum [11].

## 3. Experiment

An optical microscope image of the 2-D phase grating that was used to generate the beams for DFWM in our experiment is shown in Fig. 2. The grating was fabricated on a quartz plate using conventional photolithography and reactive ion etching (RIE). The grating period in both directions is 40 $\mu$m. The grating was designed as a 2-D binary pattern such that the optical path length difference between adjacent grating elements results in a $\pi$ phase shift at 1.5 $\mu$m. As a result, most of the diffracted beams go into the ($\pm$1,$\pm$1) orders and the (0,0) order is suppressed. The four beams in the ($\pm$1,$\pm$1) orders form the required beam geometry for our experiment. Fabrication imperfections caused the slopes seen on grating sidewalls, which results in incomplete suppression of the (0,0) order beam. The diffraction efficiency into the ($\pm$1,$\pm$1) orders

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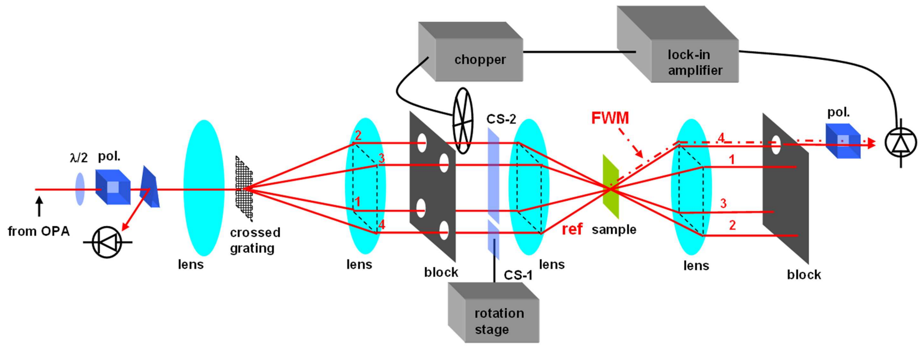


Fig. 3. Experimental setup for DFWM measurement using an imaged 2-D phase grating.

was measured using a CW laser at 1.5 $\mu$m to be 70%, which is consistent with the calculated diffraction pattern of the fabricated grating in Fig. 2.

The experimental setup is illustrated in Fig. 3. The laser source is an OPA (Spectra-Physics OPA800-C) pumped by a regenerative Ti:sapphire amplifier (Spectra-Physics Hurricane system). The system generates 130fs output pulses at 1525nm with a repetition rate of 1kHz. A half-wave plate and a polarizer are used to control the intensity. The beam is focused onto the 2-D phase grating and diffracted into four replicas ($\pm$1,$\pm$1 diffraction orders). All other diffractive orders are blocked with a mask. The beams are arranged in the folded-boxcars [12] geometry and are 1X imaged onto the sample with a telescope consisting of two identical spherical lenses with 10 cm focal length. After the sample, a spherical lens with 10 cm focal length is used to collimate the beams. The use of a 2-D phase grating ensures both phase matching and spatial and temporal overlap of the interacting beams. The use of a diffractive optical element beam splitter also allows the overlap of short pulses over their full aperture [13].

### 3.1. Direct detection of DFWM

One of the advantages in using a diffractive optical element based interferometer is the relative ease of optical alignment [14]. In traditional DFWM experiments, locating the DFWM signal is challenging since the signal is weak. In our experimental setup, since the DFWM signal is generated collinearly with beam 4, the detection system can be easily aligned by simply unblocking beam 4, and irises can be placed accurately to block the unwanted beams and scattered light.

In the direct detection experiment, the reference field (beam 4) is blocked before the sample, and the DFWM signal is generated in the direction of beam 4. Assuming the pump beams are undepleted, the DFWM signal, beam 4, after a nonlinear sample of thickness $L$ and refractive index $n$ is [15]

$$I_4 \propto \frac{|\chi^{(3)}|^2 L^2}{n^4} I_1 I_2 I_3 = m I_1 I_2 I_3, \tag{1}$$

where $m$ is a proportionality constant.

In our experiment, a reference fused silica sample with known nonlinearity $\chi^{(3)}_{ref} = 1.5 \times 10^{-14}$esu [16,17] and thickness $L_{ref} = 520\mu$m was first measured to obtain the proportionality constant $m_{ref}$. Then, the same measurement was carried out on a 100$\mu$m thick processable polyacetylene polymer to obtain $m_{sam}$. By comparing the proportionality constants, $m_{ref}$ and

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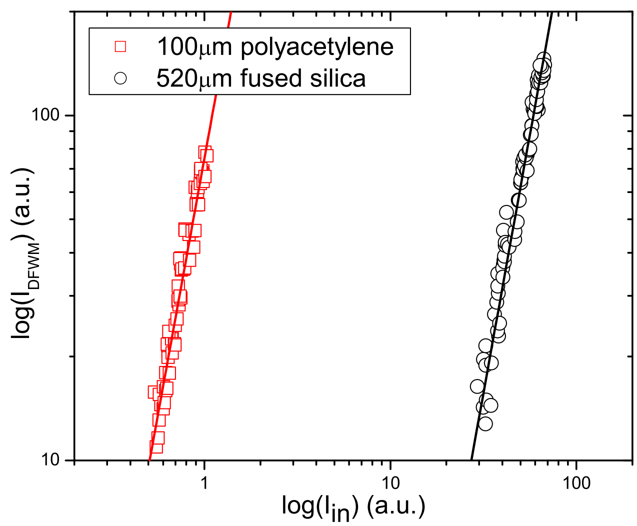


Fig. 4. Cubic dependence of the DFWM signals of polyacetylene and fused silica to the input intensity. Slopes of the linear fits are 2.97 and 3.00 for polyacetylene and fused silica, respectively.

$m_{sam}$, the absolute value of $\chi^{(3)}_{sam}$ can be calculated as

$$|\chi^{(3)}_{sam}| = |\chi^{(3)}_{ref}| \left(\frac{m_{sam}}{m_{ref}}\right)^{1/2} \frac{L_{ref}}{L_{sam}} \left(\frac{n_{sam}}{n_{ref}}\right)^{2}. \tag{2}$$

Figure 4 shows the cubic dependence of the DFWM signal to the input beam intensity for both the reference fused silica and the polyacetylene. The magnitude of the third-order nonlinearity of the nonlinear polymer is calculated to be $|\chi^{(3)}| = 7 \times 10^{-11}$esu from the measurement.

The DFWM signal of the polyacetylene sample is eliminated by introducing ~250 fs delay into one of the interacting beams using a microscope cover slip. This indicates that no slow effect (>250fs) is present, and no permanent grating is formed on the sample.

### 3.2. Coherent detection of DFWM

In the coherent detection experiment, beam 4 is unblocked and mixed with the DFWM signal on the detector. The phase between beam 4 and DFWM signal is stabilized passively with the 2-D phase grating. Beam 2 is chopped before the sample to eliminate pump-probe contamination [9]. A 150 $\mu$m thick cover slip (CS-1) is mounted on a rotation stage and inserted into the path of beam 4 to control its relative phase with respect to the DFWM signal. A matching cover slip (CS-2) is inserted into the other beam paths to ensure proper temporal overlap. The intensity of beam 4 on the detector is adjusted by a variable pinhole (not shown in the figure).

The third-order nonlinearity can be written in terms of its magnitude, $|\chi^{(3)}|$, and phase, $\phi$, as $\chi^{(3)} = |\chi^{(3)}|\exp(j\phi)$. With this expression, the coherent detection signal can be described by the following equation,

$$I = I_{DFWM} + I_{ref} + 2\sqrt{I_{DFWM} I_{ref}}\cos(\theta + \Delta\theta). \tag{3}$$

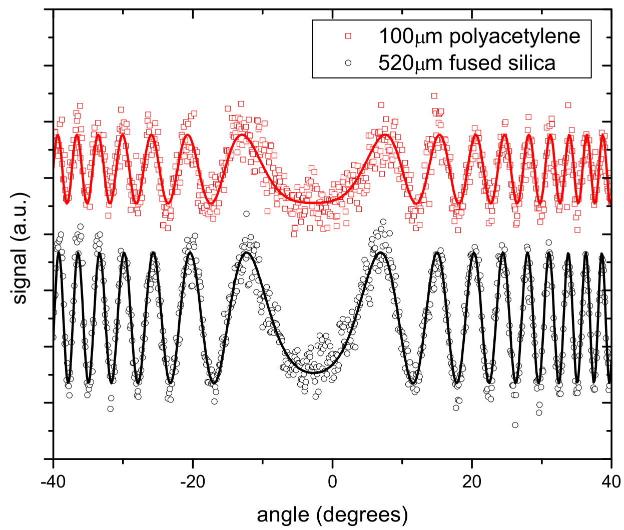


Fig. 5. Interferograms of the coherent detected DFWM signals of polyacetylene and fused silica.

$\Delta\theta$ is the phase difference between reference and signal due to cover slip rotation and $\theta = \theta_0 + \phi$. The DC signal $I_{ref}$ is removed by chopping beam 2. Rotation of the cover slip changes the path lengths of the reference beam in air and in the cover slip, which introduces a phase difference between the reference and signal beams. The phase difference $\Delta\theta$ is related to the cover slip rotation angle by [18]

$$\Delta\theta = \frac{2\pi d}{\lambda}\left[n_{cs}\left(\frac{1}{\cos\beta} - \frac{1}{\cos\beta_0}\right) - n_a\left(\frac{\cos(\alpha-\beta)}{\cos\beta} - \frac{\cos(\alpha_0-\beta_0)}{\cos\beta_0}\right)\right], \tag{4}$$

where $n_{cs}$ is the refractive index of the cover slip, $n_a$ is the refractive index of air, $d$ is the cover slip thickness, $\lambda$ is the wavelength, $\alpha$ and $\beta$ are the incident and transmission angles at the air and cover slip interface and are related by $n_a \sin\alpha = n_{cs}\sin\beta$.

The interference signals of the polyacetylene film and the reference fused silica are plotted and fit with the above expressions in Fig. 5. Since $\phi$ is assumed to be zero for fused silica, the phase constant $\theta_0$ is determined from fitting parameter $\theta$ for fused silica. With knowledge of $\theta_0$ from fused silica, the phase of the third-order nonlinearity of the nonlinear polymer is calculated to be $\phi = 21.0° \pm 1.2°$ by comparing the fitting parameters.

A 25 $\mu$m thick film fabricated in an identical manner to the 100 $\mu$m film was characterized by the Z-scan technique at 1.55 $\mu$m and the optical layout used was a standard one [1]. The resulting phase was found to be $\phi = 20.0° \pm 1.5°$ in good agreement with the results found using the coherent detection method of DFWM.

## 4. Results and discussion

From the direct and coherent measurements of DFWM signal of the polyacetylene sample, we obtained its nonlinear refractive index $n_2$ and nonlinear absorption coefficient $\alpha_2$. The nonlinear refractive index $n_2$ is defined as

$$n = n_0 + n_2 I, \tag{5}$$

where $n_0$ is the linear refractive index and $I$ is the intensity of the optical field. The parameter $n_2$ has units of m$^2$/W and is related to the real part of $\chi^{(3)}$ as [19]

$$n_2 = \frac{3\mathrm{Re}\chi^{(3)}}{4\varepsilon_0 c n_0^2}. \tag{6}$$

$\chi^{(3)}$ measured in the electrostatic units (esu) can be related to $n_2$ by

$$n_2 \left[\frac{\mathrm{m}^2}{\mathrm{W}}\right] = \frac{\pi}{3\varepsilon_0 c n_0^2} 10^{-8} \mathrm{Re}\chi^{(3)} [\mathrm{esu}]. \tag{7}$$

Similarly, the nonlinear absorption coefficient is defined as

$$\alpha = \alpha_0 + \alpha_2 I, \tag{8}$$

where $\alpha_0$ is the linear absorption coefficient. The parameter $\alpha_2$ has units of m/W and is related to the imaginary part of $\chi^{(3)}$ as [19]

$$\alpha_2 = \frac{3\omega\mathrm{Im}\chi^{(3)}}{2\varepsilon_0 c^2 n_0^2}. \tag{9}$$

$\chi^{(3)}$ in the electrostatic units is related to $\alpha_2$ by

$$\alpha_2 \left[\frac{\mathrm{m}}{\mathrm{W}}\right] = \frac{2\pi\omega}{3\varepsilon_0 c^2 n_0^2} 10^{-8} \mathrm{Im}\chi^{(3)} [\mathrm{esu}]. \tag{10}$$

From the magnitude and phase of the measured $\chi^{(3)}$ of the polyacetylene sample, we calculated the $n_2$ to be $5.3 \times 10^{-17}$ (m$^2$/W), and the $\alpha_2$ to be $1.7 \times 10^{-10}$ (m/W).

From Eq. (1) and Eq. (3), the coherently detected signal can be written as

$$I = mI_1 I_2 I_3 + I_{ref} + 2\sqrt{mI_1 I_2 I_3 I_{ref}} \cos(\theta + \Delta\theta), \tag{11}$$

where $I_1$, $I_2$, $I_3$, and $I_{ref}$ are related linearly to the incident intensity on the 2-D grating by fixed constants. With knowledge of incident intensity, the ratio of proportionality constants $m_{sam}/m_{ref}$ in Eq. (2) can be obtained from the fit parameters of the interferograms of polyacetylene and fused silica. Both absolute value $|\chi^{(3)}_{sam}|$ and phase $\phi$ can thus be obtained from coherent detection of DFWM. In this paper, we chose to perform direct detection of DFWM to verify the cubic dependence of the nonlinearity. In practice, if the order of nonlinearity is known, coherent detection of DFWM is sufficient for the characterization of complex $\chi^{(3)}$.

We analyzed the dispersion of the two lens imaging system chosen in our experiment and found the pulse broadening and the abberation of the imaged grating to be insignificant for our current application. A comparative analysis on imaging systems for grating based excitation of dynamic gratings can be found in ref. [20].

Temporal resolution of this technique can be improved by introducing variable delay into the current setup. Due to the compactness of the current optical layout, paired glass wedges as reported in ref. [21] could be a good choice for future implementation.

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## 5. Conclusion

DFWM measurement using a 2-D phase grating combines both the sensitivity of DFWM scheme and the passive phase stability using diffractive optical elements. This setup is applicable over a wide wavelength range as long as enough power is obtained in the ($\pm$1,$\pm$1) orders. The spatial and temporal overlap can be obtained easily, and passive phase stabilization can be achieved for coherent detection. Using this technique, the nonlinear refractive index and nonlinear absorption coefficient of a processable polyacetylene sample are measured. The time scale of the nonlinearity is determined to be $<$250 fs by introducing optical delay into the measurement system.


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